

1 Introduction

Hundreds of sites in the United States have been heavily polluted with organic and trace metal contaminants resulting from various activities including electroplating, metal working, battery recycling, solvent manufacturing, etc. As a result of such widespread contamination, Congress has passed legislation designed to reduce the production of pollutants, control the discharge of these species, and remediate sites where the contamination causes serious environmental problems.

Hazardous Waste Regulations

Three of the more prominent Acts promulgated by Congress include the Resource Conservation and Recovery Act (RCRA) (40 CFR 260, Subtitle C), the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (Lee 1993) (40 CFR 300), and the Federal Facilities Act (FFA) (40 CFR Subpart K) (Code of Federal Regulations 1992). Together, these laws define hazardous substances and their constituents as well as outline regulations governing the generation, transport, storage, disposal, and cleanup of these wastes.

RCRA

RCRA (promulgated in 1980) lists specific hazardous materials that must be monitored and possibly treated before disposal. These materials are separated into four categories: listed wastes, characteristic wastes, listed mixture wastes, and characteristic mixture wastes.

Listed wastes are known hazardous substances that are further divided into four categories according to the following characteristics: K-Specific, F-Non-specific, P-Acute, and U-Non-acute. K and F Listed wastes indicate whether a hazardous substance was generated from a nonspecific source or was generated through a specific process such as rinsewater from a metal-plating facility. P and U Listed wastes, refer to the toxicity level of the waste. A complete listing of these substances can be found in 40 CFR 261.32.

Characteristic wastes are those substances that exhibit the properties of toxicity, corrosivity, ignitability, or reactivity. A listed mixture waste is a listed waste that

has been combined with another substance. Like listed mixture wastes, characteristic mixture wastes are characteristic wastes that have been mixed with another substance (40 CFR 260.21).

A comprehensive United States Environmental Protection Agency (USEPA) standard toxicity characteristics leaching procedure (TCLP) is performed on some types of waste or soil samples collected from process streams or soils that are suspected of posing ecological risk. If any of the hazardous constituents of the waste are present in the TCLP extract in concentrations that exceed the minimum concentration level established by the USEPA, the waste must be disposed of in an RCRA-approved hazardous waste landfill. State and local authorities can further stipulate more stringent cleanup criteria. In many instances, a contaminated soil can pass the Federally mandated TCLP, but fail to meet the minimum concentration standards mandated by State agencies.

The Hazardous and Solid Waste Amendments substantially modified RCRA regulations in 1984. According to these regulations, the contaminated material that is removed from a site cannot be disposed in a landfill unless it has been treated to meet certain cleanup standards. These regulations may pose a problem for site remediation activities that use the “dig and haul” approach since, in many instances, the contaminated material is currently being excavated and sent to an RCRA-approved landfill without any treatment.

CERCLA

CERCLA, also referred to as Superfund, addresses sites that are already contaminated with hazardous materials. CERCLA outlines a ranking scheme to determine the health and environmental risks associated with hazardous waste. If the risks are significant, the site will be prioritized on the National Priority List (NPL). NPL sites are considered to be the most contaminated sites thus receiving priority attention and cleanup actions. The financial responsibility of site remediation is assumed by potentially responsible parties, which refer to those persons or industries that are responsible for the pollution.

FFA

In an effort to address widespread contamination at U.S. Department of Energy (DOE) and Department of Defense (DOD) sites, Congress added a special section to CERCLA known as the Federal Facilities Act. This Act established a listing of the most heavily contaminated Federal sites based on many of the same factors used in NPL rankings. To fund cleanup of these sites, DOE and DOD established the Defense Environmental Restoration Program funded by Congress through the Defense Environmental Restoration Account (Lee 1993). As required by RCRA, CERCLA, and FFA, industrial and Federal sites contaminated with hazardous materials must develop strategies for site remediation.

Overview of Current Soil Treatment Technologies

The U.S. Army Engineer Waterways Experiment Station (WES) is responsible for developing treatment technologies under the Army's installation restoration program to assist in remediation of Federal facilities contaminated with hazardous substances (Bricka, Williford, and Jones 1993). Although the cleanup of numerous hazardous materials is being investigated, the Army has recognized that heavy metals contamination deserves a greater allocation of military resources because of its predominance at Army sites and the lack of technology to address such contaminants.

The majority of historical metal contamination at military sites is found in firing range soils, ammunitions manufacturing facilities, weapons manufacturing facilities, and electroplating and metal workshop areas, as well as incineration rinse-water lagoons and weapon and debris disposal areas. In fact, heavy metals currently constitute five of the six most cited hazardous materials at Army sites (Bricka, Williford, and Jones 1993). Metals frequently found at military sites are lead (Pb), cadmium (Cd), and chromium (Cr). All of these metal elements are toxic to human health causing a variety of ailments including brain/ neurological damage, liver and kidney damage, and cancer (*Technological Profile for Cadmium Draft* 1987; *Technological Profile for Chromium Draft* 1987). Their contaminant pathways include ingestion of contaminated water, soil ingestion usually resulting from poor hygiene, soil absorption through the skin, and dust/vapor inhalation.

To address these threats to human health, a limited number of technologies have been developed for treating and/or disposing of soils polluted with heavy metals. The advantages and disadvantages of some of the more pertinent technologies are discussed in the following sections.

"Dig and haul"/landfilling

Perhaps the most widely used remediation technique involves excavating soils contaminated with hazardous materials and disposing of the contaminated soils off-site, usually in RCRA-approved landfills. Currently, the cost of disposing contaminated soils in a hazardous waste landfill ranges approximately between \$2,000 and \$2,500 per cubic yard (Bricka, Williford, and Jones 1993). Stringent regulations governing the operation of hazardous waste landfills and dwindling landfill space are constantly increasing the cost of burying contaminated soil, thereby making this alternative less desirable. Additionally, monitoring of soil and groundwater at the landfill will still be necessary, making the cost of implementing such a strategy more prohibitive (Royer, Selvakumar, and Gaire 1991). More alarming than the costliness of the technology is the fact that the landfilling approach remains flawed because contaminants are merely transferred from one site to another. With dig and haul techniques, contaminants in the soil do not undergo any treatment to be either immobilized or kept from leaching from the soil.

Soil capping

Capping uses a cover placed over contaminated soil sites to reduce off-site contaminant migration. Either a single-layer or multilayer system of highly impermeable synthetic membranes or clay layers can be used for capping the contaminated soil. This cap prevents infiltration of precipitation into the contaminated site, thus preventing the water from percolating through the waste providing a pathway to potentially contaminate groundwater supplies. Full site containment and economic feasibility are two major advantages of the soil capping technique (Royer, Selvakumar, and Gaire 1991). However, as with landfilling, the contaminants in the capped waste are neither treated nor removed.

Solidification/stabilization

Solidification/Stabilization (S/S) is a technology with full-scale application that does involve treatment of the contaminated soil. Contaminated soils are mixed with binding agents such as cement, fly ash, pozzolanic concrete, lime, or kiln dust. In many S/S processes, monolithic blocks are produced with enhanced chemical and physical characteristics. This treatment is designed to immobilize the hazardous contaminants.

The binding agents perform two functions. First, the chemicals within the binding agents immobilize soluble metals through partial chemical bonding. The new soil matrix reduces the potential for leaching of substances into groundwater supplies. Second, the binding agents alter the physical properties of the soil by increasing strength and decreasing compressibility and permeability. Since the pH of the binding agents is usually high, remobilization of metals from hydroxide and carbonate salt states is very unlikely (LaGrega, Buckingham, and Evans 1994).

A variety of tests can be performed on the solidified material to measure both its chemical and physical nature after stabilization. Some of these tests include the TCLP and the Sequential Leach Test, which measure the leachability of the contaminants, as well as the Cone Index and the Unconfined Compressive Strength Tests, which gauge the material's strength and ability to handle large pressure loads (LaGrega, Buckingham, and Evans 1994).

Studies at several contaminated sites monitored by the USEPA have shown that S/S effectively immobilized contaminants in soils (Royer, Selvakumar, and Gaire 1991). Although this technique reduces the mobility of contaminants, its application has two major concerns. First, metals are not removed from the soil, thereby providing the potential for contaminant migration in the future. Thus, the generator of the waste is left with long-term liability. Second, binding agents may break down after several years leading to contaminant remobilization. If this occurs, the soil will either have to be resolidified or remediated with alternative techniques.

Vitrification

Vitrification (or glassmaking) stabilizes trace metals in soils through the conversion of contaminated soil into basalt glasslike, noncrystalline materials using high temperature meltdown followed by rapid cooling (Royer, Selvakumar, and Gaire 1991). This high temperature thermal conversion is achieved by placing electrodes into the soil while graphite and glass frit are placed on top of the soil to serve as starter materials. A current is applied to the graphite and embedded electrodes creating a high temperature zone that causes meltdown of the soil at a rate of 4 to 6 tons¹ per hour (LaGrega, Buckingham, and Evans 1994). Once the soil cools, contaminants are permanently retained in glass forms. Volume reduction is a major advantage of the vitrification technique. When heat is applied, the liquid in the soil is evaporated, thus reducing the original volume of contaminated soil. In addition, the vitrified soil is highly resistant to contaminant leaching; however, the process does require a great amount of energy to achieve desired temperatures for meltdown, and the soil matrix is destroyed instead of being salvaged.

Ion exchange

Ion exchange is a treatment process in which metals in solution are substituted with exchangeable ions from either synthetic resins or clays. These resins and clays usually have high exchange capacities because their ion functional groups easily bind with cationic ions in the contaminated solution (Royer, Selvakumar, and Gaire 1991). The ion exchange process can be easily implemented. First, the solution and resin (or clay) are mixed, leading to an exchange between less harmful ions in the medium with metal ions contained in solution. This can be implemented using a column or batch process. In a batch process, the solution and solid are separated through sedimentation or centrifugation. This process is widely recognized in water softening applications where sodium (Na^+) ions in the resin replace calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in the water that cause hardness. Factors that affect this process include pH, cation competition, and the presence of complexing agents.

To initiate ion exchange in the field for soil remediation, synthetic or clay mediums are introduced into the soil through creation of a slurry containing both contaminated soil and medium (Bricka, Williford, and Jones 1994). After a suitable contact time, the resins that contain high concentrations of contaminants are removed. Advantages of this process include commercial availability of processing units, low energy costs, and the potential regeneration of synthetic resins. The major disadvantage of ion exchange is associated regeneration or disposal costs if regeneration is not possible or cost prohibitive (Royer, Selvakumar, and Gaire 1991).

¹A table of factors for converting non-SI units of measurement to SI units is presented on page ix.

Electrokinetics

Electrokinetic remediation of soil is a rapidly emerging and potentially cost-effective technology that centers on the use of an electrical potential to move charged contaminants toward electrodes of opposite charge. Graphite or other conducting metal electrodes are placed in situ on either side of the contaminated soil mass. Through current application, an acidic front is propagated at the anode and assists in the release of soluble metals into the pore fluid. Simultaneously, a basic front is created at the cathode that moves toward the anode. Amendments are added to the cathode to keep soil pH below 7 in this remediation system to reduce soil pore clogging caused by metal precipitation (Hamed, Acar, and Gale 1991). The electrode fluid having elevated concentrations of metals is extracted and treated to remove the contaminants (Hamed, Acar, and Gale 1991).

Soil washing

Unlike processes that reduce the leachability of contaminants, soil washing focuses on chemical leaching to remove metals from contaminated soil. This process of leaching contaminants from the soil particles into solution is generally achieved through two distinct processes: (a) physical separation of the contaminated soil particles, and (b) chemical extraction of the metal contaminants. Physical separation reduces the volume of soil that has to be chemically treated. Chemical extraction breaks the metal-soil bonds, forcing contaminants into solution. A detailed description of the two mechanisms is outlined below.

Physical separation. Physical separation processes attempt to separate soil fractions using differences in particle size, density, surface area, and magnetism (Bricka, Williford, and Jones 1994). In general, particles with small diameters have the ability to retain or adsorb a greater quantity of metals per unit weight of soil particles because they have relatively large surface areas that are capable of metal bonding.

The physical separation process begins with a characterization of the soil to determine the location and extent of contamination. Samples of the contaminated soil are thoroughly homogenized to ensure uniform distribution of particles and contaminants. Once homogenized, the soil is separated into distinct size fractions.

The separation process is accomplished through several stages beginning with an initial screening to remove oversized particles. The remaining fraction is further processed to isolate finer fractions using mechanical shaking sieves or trommel screens. The particles that pass through the sieve or screen are further classified, while the larger particles are removed for disposal or onsite backfilling, depending on their contamination level. Separation of the fine particles can be accomplished using equipment that includes spiral concentrators or hydrocyclones.

If separation is effective in concentrating the metal contaminants in a smaller soil volume, the less contaminated soil is backfilled; the concentrated fraction can then be treated using chemical extraction techniques.

Chemical extraction. Chemical extraction, the focus of this study, is a process in which the contaminated soil is mixed with an extracting agent or solvent that is capable of desorbing the contaminant from the soil particle surface into solution. Usually, only the most heavily contaminated soil fraction is treated by use of the chemical extraction process, due to the cost associated with this treatment.

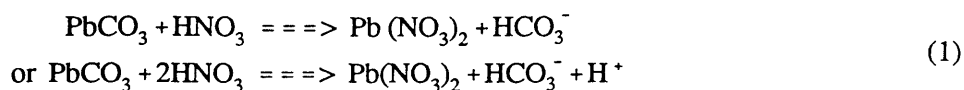
Both organic and metal contaminants in soil can be removed by use of the extraction processes by tailoring the process using organic solvents, acids, chelating agents, or supercritical fluids. In the case of organic contaminant removal, solvents such as ethanol and acetone are used to desorb the contaminants from the organic matter (Piersynski, Sims, and Vance 1994; Markiewicz and McGovern 1992). Acids, bases, and chelating agents are the major extracting agents used to leach metal contaminants from soil. These chemicals react to solubilize metals that are bound to various soil fractions. Acids solubilize metals through ion exchange, while chelating agents solubilize metals through complexation.

For effective metal removal, the contact period between soil particles and the extracting agent should be sufficient for the chemical reactions to approach equilibrium. Once contaminant transfer reaches equilibrium, mixing and reaction are ceased, and the solids and liquid are separated using treatments that include filtration, centrifugation, or reverse osmosis. The metal-enriched solution can be further concentrated or recycled depending on the metals content.

Numerous studies have been devoted to the subject of chemical equilibrium between metal contaminants in soils and extracting agents. For example, when extracting metals from contaminated riverbed sediment using magnesium chloride (MgCl_2) and hydrochloric acid (HCl), Trefry and Metz (1984) found that the reaction time to reach equilibrium was less than 12 hr for Cd, copper (Cu), and zinc (Zn), while more time was needed to reach equilibrium for Pb. In contrast, Peters and Shem (1991) determined that metal removal was dependent on the type of extracting agent used. Using a spiked soil, Peters determined the time to reach equilibrium for ethylenediaminetetraacetic acid (EDTA) and Pb was 1 hr, while the reaction between nitrilotriacetic acid (NTA) and Pb reached equilibrium in 3 hr. These findings indicate that soil-extracting agent equilibrium may depend on several factors, including the type of soil, type and concentration of extracting agent, and soil contaminant.

Since this research focuses on the removal of metals from contaminated soil, the function of acids and chelating agents as metal extracting agents is further explored.

Acids. Acids dissociate in aqueous solution to become proton donors. When mixed with a metal-contaminated soil, these protons replace or exchange with the metal ions that are bound to the soil. Equation 1 is a typical example of an acid extraction involving Pb^{2+} sorbed to the carbonate fraction of soil mixed with nitric acid (HNO_3):



Typical acids used in metal extraction include HNO_3 , HCl , and hydrofluoric acid (HF). Although acids effectively increase the solubility of metals, strong acids tend to destroy the basic structure of the soil (Bricka, Williford, and Jones 1993). This destruction of the soil matrix can leave the soil unsuitable for revegetation and reuses. Given the potential destructive nature of acids, much research has been devoted to chemicals that can extract metals with little effect on the soil structure.

Chelating agents. Chelating agents (chelates) form stable complexes with metals. The strength of the resulting complex depends on the number of rings or sites, attachment on the coordination compound, and the type of metal species present. Chelating agents that attach at only one point are called monodentate ligands, while those with more than one attachment site are referred to as multidentate ligands. When contacted with metals bound to soil particles, the functional groups or sites on the chelate bind with the metals sorbed to the soil surfaces. Since the metal will usually have a greater affinity for chelate site attachment than soil attachment, a net solubilization of the metal species occurs. EDTA is an example of a multidentate ligand that has six sites for attachment (Figure 1). It can form up to six complexes with metal ions on its four acetate groups and two nitrogen atoms that hold free electron pairs (Snoeyink and Jenkins 1980). In addition to EDTA, other typical chelating agents used for metal extraction and soil washing include (NTA), diethylenetriaminepentaacetic acid (DTPA), and citric acid.

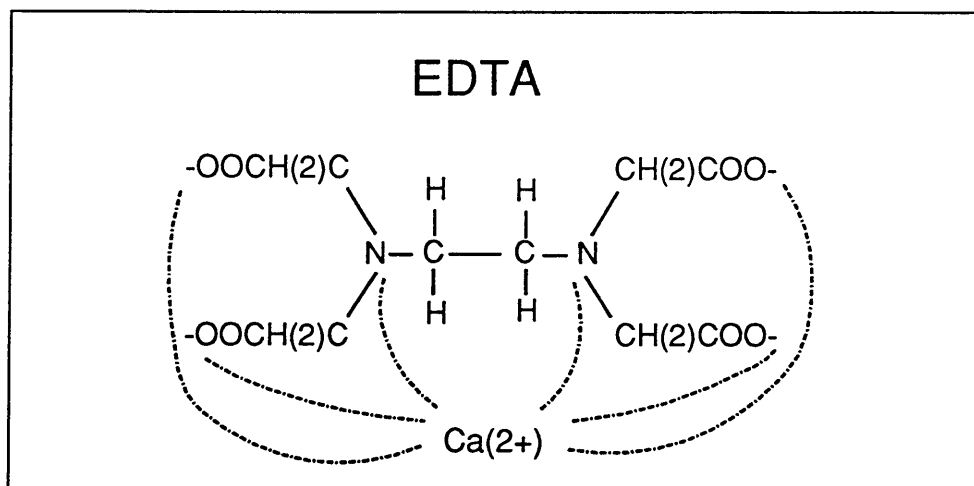


Figure 1. EDTA site attachment (after Snoeyink and Jenkins 1980)

Properties affecting extraction. Some properties of soil and contaminants, specifically metals, can significantly affect the ability of an extracting agent to leach metals or other contaminants from soil. Among the more important properties are cation exchange capacity (CEC), pH, total organic carbon (TOC), and soil chemical phase groups.

Cation exchange capacity. CEC refers to the number of exchange sites within a soil that can sorb cations (Pierzynski, Sims, and Vance 1994). The number of exchange sites on clay soil particles can remain constant or fluctuate with changes in pH. Stable sites result from natural electrostatic forces within soil, while pH-dependent sites typically increase with an increase in pH (Brady 1974). Most trivalent metals such as aluminum (Al^{3+}) generally have a greater affinity for these sorption sites than divalent and monovalent cations (Brady 1974). In most cases, soils with a larger fraction of humus or organic material will have a larger number of cation exchange sites. Table 1 outlines some of the major types of soils in the United States and their respective CEC values. The values indicate that sand particles have the smallest CEC, while clay and clay loam particles have the greatest CEC. The table also reveals that CEC can widely vary within a soil type as evidenced by the two soils characterized as clay and clay loam. Soils can also have an anionic exchange capacity (AEC) if the charges on the soil particles are positive as opposed to negative.

Table 1 CEC of Major United States Soils		
Soil Description	Soil Type	CEC, meq/100 g of dry soil
Sand	Plainfield, WI	3.5
Sandy Loam	Norfolk	3.0
Sandy Loam	Cecil, SC	5.5
Loam	Hoosic, NJ	11.4
Loam	Dover, NJ	14.0
Silt Loam	Dawes, NE	18.4
Silt Loam	Carrington, MN	18.4
Clay and Clay Loam	Cecil clay, AL	4.8
Clay and Clay Loam	Gleason clay loam, CA	31.5
Note: after Brady (1974).		

pH. The relative acidity or basicity of a soil can either increase or decrease the strength of bonds between soil and trace metals. In acidic soil, most of the binding sites on the soil are dominated by protons. The resulting hydrogen-soil bonds are highly resistant to cation exchange (Brady 1974). On the other hand, the exchangeable sites of soils that are naturally basic are attached to exchangeable ions like Ca^{2+} , Mg^{2+} , and potassium (K^{+}). Basic soils are usually amenable to cation exchange and therefore have a higher CEC. As a result, it is often useful to increase the pH of a soil to increase the rate of cation exchange. This increase can be easily accomplished by tilling a powdered lime ($Ca(OH)_2$) slurry into the soil (Brady 1974).

Total organic carbon. The amount of TOC within a soil greatly enhances the absorption of metal cations. Organic or humic soil material has an extremely high surface area and therefore has a greater number of exchange sites than other soil particles. These ion functional exchange sites are usually attached to protons; however, increases in pH can result in dissociation of the soil surface site and H^+ , thus freeing sites that are available for adsorption by other cations (Bohn, McNeal, and O'Conner 1985).

Surface area. The total surface area of a soil can affect its sorption of metal contaminants. Smaller clay particles have a much greater surface-to-volume ratio and thus have more area for contact with extraction fluids than do larger sand particles. They also contain higher concentrations of contaminants than the sand particles.

Soil components and solubilities of metal compounds. The extractability of metal ions from soil or the rate of metal extraction is also influenced by the type of soil components, or the negatively charged fractions of the soil that can serve as attachment sites for cationic species (Manahan 1994). For example, metals are most easily removed from soils that contain a high percentage of carbonates, whereas removal of metals from soils with high clay mineral content may be difficult (Bricka, Williford, and Jones 1993). The difference is caused by the relative strength of bonding between metals bound to carbonates versus metals bound to the clay mineral fraction of the soil. Table 2 summarizes the ease of extraction of cationic metals from five soil components.

Table 2 Comparison of Chemical Phase Soil Groups	
Chemical Phase Soil Groups	Ease of Metal Removal (Ranking of 1 = easiest rate of removal)
Carbonates	1
Iron and Manganese Oxides and Hydroxides	2
Organic Matter	3
Sulfides	4
Clay Minerals	5
Silicates	Unknown
Note: Bricka, Williford, and Jones (1993); Tuin and Tels (1990a).	

The solubility of metal compounds also plays a critical role in the extractability of metals. For example, nitrates are highly soluble in water; therefore, HNO_3 might be an effective extracting agent. When HNO_3 is applied, H^+ ions displace the metal cations in the soil matrix, resulting in the formation of highly soluble metal-nitrate salts that will remain in solution and will not become reentrained in the soil matrix as a precipitate.

Table 3 lists some common metallic compounds and their solubilities in aqueous solution. This table contains useful information for the screening of potential extracting agents to be used in soil washing applications.

Table 3 Generalizations on Solubilities of Metallic Compounds
Nitrates and acetates are soluble in water; silver acetate, chromium (II) acetate, and mercury (I) acetate are slightly soluble.
Chlorates are soluble in water except potassium chlorate, which is slightly soluble.
Chlorides are soluble except mercury (I), silver, lead, and copper (I) chloride; lead chloride is soluble in hot water.
Sulfates except for strontium, barium and lead sulfate are soluble; calcium sulfate and silver sulfate are slightly soluble.
Carbonates, phosphates, borates, arsenates, and arsenites are insoluble except those of ammonium and the alkali metals.
Sulfides of ammonium and alkali metals are soluble, while other sulfides are not; alkaline earth metal sulfides become hydrolyzed in water.
Hydroxides of sodium, potassium, ammonium, barium, and strontium are soluble, while other hydroxides are not; calcium hydroxide is slightly soluble.
Note: after Nebergall, Schmidt, and Holtzclaw (1976).

Background

Several studies have attempted to optimize the metal extraction process using acids, bases, and chelating agents. These studies have investigated the different types of parameters that might affect metal extraction including soil-to-extracting agent ratio, types and concentrations of extracting agents, and contact time.

Argonne National Laboratories and chelating agents

Dr. Robert Peters of Argonne National Laboratories (Peters and Shem 1991) has done extensive research on the complexation of metals through the use of a variety of chelating agents. In selecting the best chelating agents to use in testing, Peters developed five major selection criteria:

- a. Reagents that form stable complexes over wide pH range at 1:1 ligand-to-metal molar ratio.
- b. Low biodegradability of complexing agents and complexes.
- c. Metal complexes are nonadsorbable.

- d. Low environmental harm of chelating agents.
- e. Cost-effectiveness.

The agents that best meet these criteria and that have been extensively studied are EDTA, NTA, and DTPA.

The majority of Peters' laboratory testing focused on EDTA and NTA. His experiments used uncontaminated soil spiked with 10,000 ppm Pb and then treated with chelate concentrations of 0.01 M, 0.05 M, and 0.1 M of EDTA and NTA. Other testing parameters used in Peters' experiments include variation of pH and a general contact time of 30 min. Table 4 summarizes the resulting Pb removal efficiencies.

Table 4 Comparison of Pb Removal Rate Using EDTA and NTA			
Chelating Agent	Concentration, M	pH	Percent of Pb Removal
EDTA	0.1	6	61
NTA	0.1	6	4
EDTA	0.1	8	60
NTA	0.1	8	2
EDTA	0.1	10	58
NTA	0.1	10	11
Note: Peters and Shem (1991).			

The data shown in Table 4 reveal that 0.1 M EDTA was much more effective for Pb removal than 0.1 M NTA, regardless of pH. Peters' studies of chelating agents have also led to other observations:

- a. EDTA easily removes Cd.
- b. Solid-to-liquid ratio of 0.11 is optimal for both reagents.
- c. EDTA and Pb reach equilibrium in 1 hr.
- d. NTA and Pb reach equilibrium in 3 hr.
- e. Higher temperatures may speed solubilization of metals.
- f. Cr removal increases with increase in pH.

EDTA and HCl experiments

Tuin and Tels (1990b) also conducted experiments to study the effectiveness of EDTA as a metal-complexing agent. They used a two-stage extraction process in which contaminated soils were contacted with 0.1 N HCl followed by 0.1 M EDTA. The contact time for these experiments was 1.5 hr with a solid-to-liquid ratio of 0.05 as compared to Peters observation of 0.11 (weight/weight basis). Table 5 summarizes their results of Pb extraction from clay soils at two industrial waste sites. The percent removal of Extraction 2 represents the amount of metal extracted from the soil using the quantity of metal remaining in the soil after Extraction 1.

Table 5 Metal Extraction From Contaminated Industrial Waste Sites			
Soil Location	Target Metal	Extraction 1 Percent Removal 0.1N HCl	Extraction 2 Percent Removal 0.1M EDTA
Sophia	Cd	50	13
	Cr	16	--
	Pb	52	61
Melchior	Cd	50	17
	Cr	5	3
	Pb	53	72
Note: Tuin and Tels (1990b).			

The results show that a sequential extraction using two solutions generally improved Pb, Cd, and Cr removal in both soils tested.

Comparative complexation tests

Elliott and Brown (1989) have also conducted comparative tests to evaluate the extraction capabilities of EDTA and NTA. Their study focused on the percent removal efficiency of the two chelating agents when mixed with a soil contaminated with 211,000 mg/kg Pb at varying pH.

Using a solid-to-liquid ratio of 0.04 (weight/weight basis) and contact time of 5 hr, these results (Table 6), like the results from Peter's work, show that Pb removal using EDTA was greater than removal using NTA. EDTA was generally a more effective extracting agent than NTA because the stability constant of Pb-EDTA²⁻ (18.0) is much greater than that of Pb-NTA⁻ (11.4). Pb removal efficiency of EDTA ranged from 34 percent at pH = 10 and a concentration of 0.02 M to 95 percent at pH = 4 and a concentration of 0.08 M. Pb extraction using NTA ranged from 11 percent at pH = 12 and a concentration of 0.01 M to 62 percent at pH = 10 and a concentration of 0.06 M.

Table 6
Percent Removal of Pb From Contaminated Soil

Chelating Agent	Concentration, M	pH	Percent Pb Removal
EDTA	0.02	4	45
EDTA	0.02	6	45
EDTA	0.02	8	38
EDTA	0.02	10	34
EDTA	0.02	12	38
EDTA	0.04	4	--
EDTA	0.04	6	68
EDTA	0.04	8	64
EDTA	0.04	10	65
EDTA	0.04	12	60
EDTA	0.06	4	89
EDTA	0.06	6	81
EDTA	0.06	8	75
EDTA	0.06	10	67
EDTA	0.06	12	70
EDTA	0.08	4	95
EDTA	0.08	6	82
EDTA	0.08	8	76
EDTA	0.08	10	67
EDTA	0.08	12	65
NTA	0.01	4	--
NTA	0.01	6	22
NTA	0.01	8	20
NTA	0.01	10	15
NTA	0.01	12	11
NTA	0.02	4	--
NTA	0.02	6	35
NTA	0.02	8	28
NTA	0.02	10	25
NTA	0.02	12	20
NTA	0.04	4	--
NTA	0.04	6	59
NTA	0.04	8	53
NTA	0.04	10	47
NTA	0.04	12	30
<i>(Continued)</i>			

Table 6 (Concluded)			
Chelating Agent	Concentration, M	pH	Percent Pb Removal
NTA	0.06	4	--
NTA	0.06	6	40
NTA	0.06	8	45
NTA	0.06	10	62
NTA	0.06	12	42
NTA	0.08	4	--
NTA	0.08	6	27
NTA	0.08	8	34
NTA	0.08	10	60
NTA	0.08	12	46
Note: Elliott and Brown (1989), Elliott et al. (1989).			

A study by Norvell (1984) compared the metal extraction efficiency of EDTA, NTA, and DTPA. Using a solid-to-liquid ratio of 0.2 (weight/weight basis), the extraction tests were performed on soils contaminated with a variety of trace metals. Analyzing the extracting agents for each metal, Norvell ranked the extraction effectiveness of each chelating agent versus the target metal. His results are shown in Table 7.

Table 7 Effectiveness of EDTA, NTA, and DTPA Versus Target Metals		
Target Metal	Expected Rank	Observed Rank
Al	DTPA > NTA > EDTA	NTA > DTPA > EDTA
Zn	DTPA > EDTA > NTA	DTPA = EDTA = NTA
Cu	DTPA > EDTA > NTA	DTPA = EDTA = NTA
Cd	DTPA > EDTA > NTA	EDTA = DTPA = NTA
Note: Norvell (1984).		

Table 7 indicates that the theoretical order of the chelating agents by effectiveness were contradicted by the observed removal. EDTA, NTA, and DTPA were equally effective in removing Zn, Cu, and Cd, while NTA was more effective in removing Al.

Acid extraction comparison of HNO₃ and HCl

A number of studies have been conducted to determine the metal extraction efficiency using only strong acids. One such study was performed by Mortazavi, Volchek, and Whittaker (1992) on a soil contaminated with various metals. The soil and extracting agent were mixed for 3.5 hr. Results from this study are in Table 8.

Table 8 Extraction Test Using HCl and HNO₃				
Acid, 0.1M	Percent Removal of Cd	Percent Removal of Cu	Percent Removal of Zn	Percent Removal of Pb
HCl	54	23	80	33
HNO ₃	39	58	50	66
Note: Mortazavi, Volchek, and Whitaker (1992).				

These results show that both HCl and HNO₃ are fairly effective extracting agents depending on the metals targeted for removal. Table 8 also illustrates the importance of the solubility of the resulting metallic salts. According to Table 3, Cu (I)-chlorides and Pb-chlorides are insoluble in water, whereas Cu-nitrates and Pb-nitrates are soluble in water. Thus, it is expected that HNO₃ will be a better extracting agent than HCl for the removal of both of these metals. The results shown in Table 8 validate these findings since the removal percentages of Cu and Pb were higher using HNO₃ as the extracting agent than HCl. Table 8 also indicates that HCl had a better removal rate for Cd and Zn than HNO₃.

Neuhauser and Hartenstein (1980) also studied the metal extraction effectiveness of HCl on anaerobic sludges. In their experiment, a solid-to-liquid ratio of 0.033 (weight/ weight basis) was used with a mixing time of 1 hr. Their results (Table 9) indicate that, in general, HCl was effective at removing metals from anaerobic sludge. In particular, 1 M HCl was a better extracting agent than 0.1 M HCl for all metals tested, although nickel and cadmium removal percentages were not appreciably different.

Other laboratory tests

A variety of other chemical compounds have been evaluated as metal extracting agents. The U.S. Bureau of Mines has successfully used fluorosilicic acid to leach Pb from spent battery casings (99-percent removal) (Royer, Selvakumar, and Gaire 1992). Strong bases like sodium hydroxide (NaOH) have also been investigated for their extraction potential as a result of the amphoteric nature of metals in soil that are soluble at both high and low pH values. Assink (1985) asserted that NaOH

Table 9
Percentage of Total Metals Extracted From Anaerobic Sludge

Metal	Concentration, ppm	Percent Removal 1M, HCl	Percent Removal 0.1M, HCl
Cadmium (Cd)	96	67.9	65.3
Copper (Cu)	973	47.8	15.9
Nickel (Ni)	814	26.6	21.1
Lead (Pb)	735	66.0	37.4
Zinc (Zn)	4,202	93.0	71.3
Chromium (Cr)	1,949	55.6	26.0
Note: Neuhauser and Hartenstein (1980).			

dissolves or disperses metal contaminants during extraction, especially those contaminants in the clay or humus soil fractions.

Pilot-Scale Mobile Soil Washing Operations

Recognizing the potential for implementing soil washing technologies in the field, many private industries have tried to develop soil washing systems for remediating soils contaminated with hazardous wastes. Some of these systems focus exclusively on the removal of organic contaminants, while others use soil washing technologies to remove both organics and trace metals. In fact, most of these systems have been demonstrated at Superfund sites through the USEPA's Superfund Innovative Technology Evaluation (SITE) program. Some of the more effective soil washing units are profiled in the following sections along with a summary of their treatment effectiveness.

BioTrol soil washing system

The BioTrol soil washing process is one of the soil washing treatment technologies that has been evaluated by USEPA through a SITE demonstration. As shown in Figure 2, the BioTrol system is composed of several processes that either separate particles based on their size and density or chemically extract contaminants from soil. In this process, contaminated soil is first mixed with water in a trommel to form a slurry. The soil is then sent to a countercurrent attrition/classification circuit. This circuit produces three effluents including fine oversized material, washed soil, and wasted process water containing suspended fine particles. The washed soil represents the end product of the system, while the wasted process water suspension is sent to a thickener to dewater the fine particles and solidify them into a particle cake. Both the filter cake and the leftover fine particles and oversized material must be properly treated or disposed (Stinson, Skovronek, and Ellis 1992).

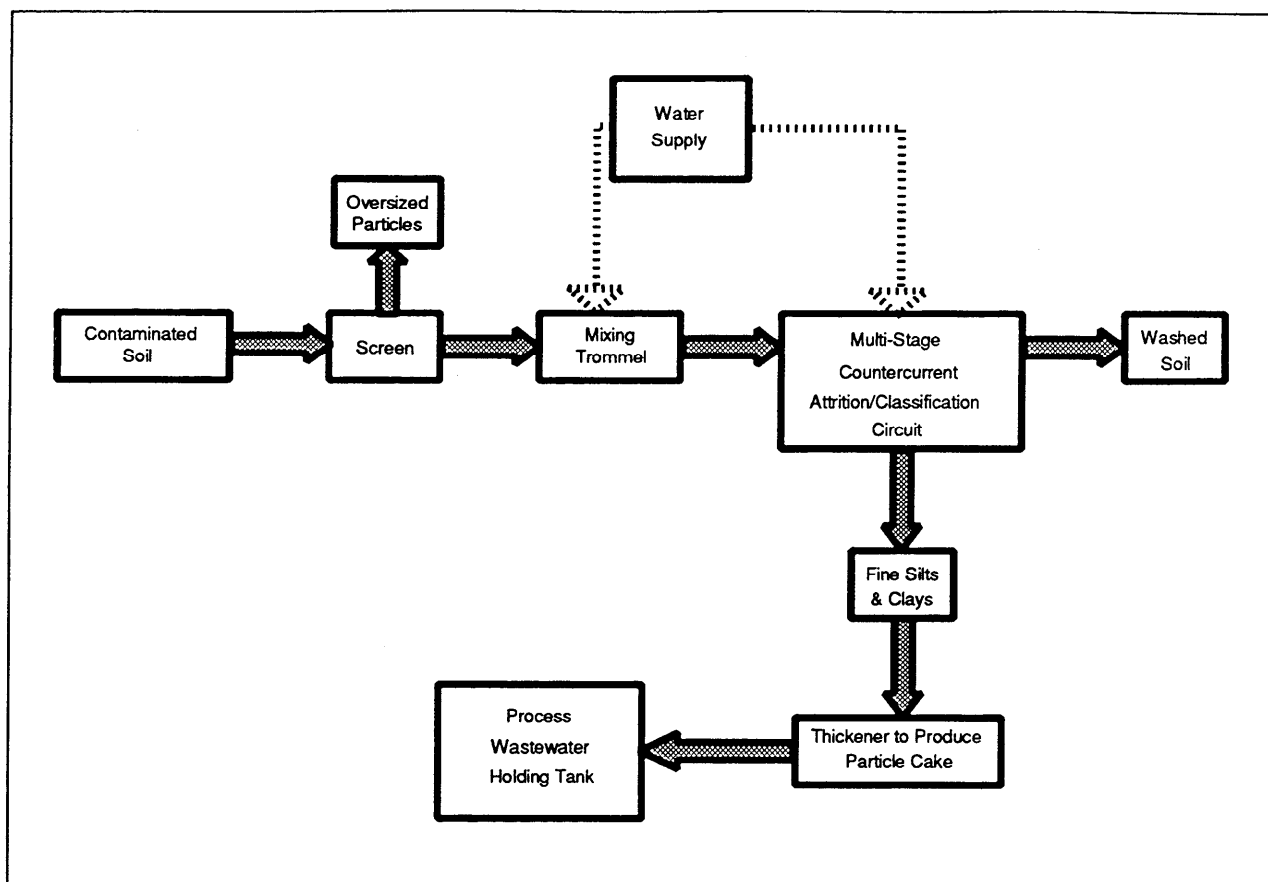


Figure 2. BioTrol soil washing process (after Stinson, Skovronek, and Ellis 1992)

The BioTrol process was used in a SITE demonstration at the MacGillis and Gibbs Superfund site in New Brighton, MN. This site formerly housed a wood-preserving facility and was heavily contaminated with pentachlorophenol (PCP), polynuclear aromatic hydrocarbons (PAHs), and trace amounts of Cr (Stinson, Skovronek, and Ellis 1992).

Two test runs were completed to determine the effectiveness of the BioTrol process. The first test run produced an 89-percent reduction of PCP, an 80-percent reduction of carcinogenic PAHs, and a 48-percent reduction of Cr. The second test run produced slightly higher reduction percentages: 87-percent reduction of PCP, 87-percent reduction of carcinogenic PAHs, and 64-percent reduction of Cr (Stinson, Skovronek, and Ellis 1992).

Cognis/Bescorp Terramet soil washing plant

Another promising soil washing system has been developed through the collaborative efforts of two companies: Cognis, Inc., of Santa Rosa, CA, and Bescorp, Inc., of Fairbanks, AK. As with the BioTrol system, the operation of the Cognis/Bescorp Terramet plant is divided into a physical separation phase and a chemical

extraction phase. Figure 3 shows the contaminated soil feeding into a trommel, which agitates the soil to remove oversized particles and to break up any agglomerated soil lumps. The oversized material is sent to an ordnance-removal conveyor, while the soil fraction that passed through the trommel is sent to a separation chamber to be further classified into sand and fines fractions. The sand and fines fractions are separately sent through a four-stage countercurrent leaching process to remove metal contaminants from the soil. The washed soils are dewatered and then recombined with the oversized fraction. The mixture is neutralized and returned to the original site.

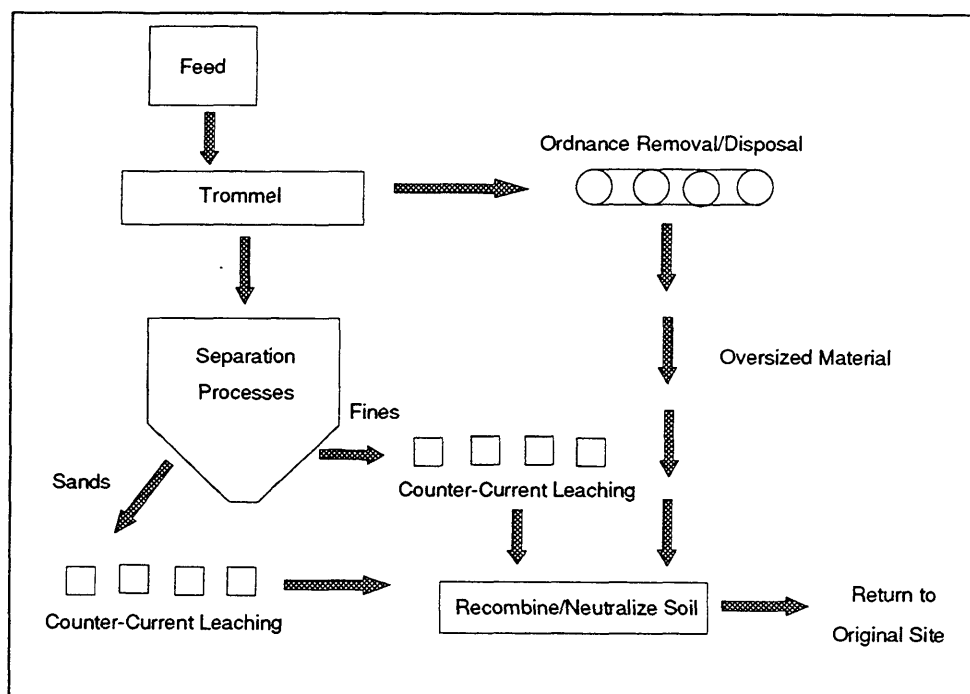


Figure 3. Cognis/Bescorp Terramet soil washing plant (after COGNIS 1993)

Since 1993, the Cognis/Bescorp Terrament Soil Washing Plant has been used to remediate contaminated soil from Site F of the Twin Cities Army Ammunition Plant (TCAAP) in Arden Hills, MN. Most of the contamination at this site resulted from open burning, ammunitions burial, and open detonation of explosives. Remediation of the site has been especially challenging since trace metal contamination had to be restored to naturally occurring background levels. However, the Cognis/Bescorp system has been able to meet all of the cleanup criteria as mandated by USEPA and the Minnesota Pollution Control Agency for the majority of the soil processed. Some of the cleanup results are summarized in Table 10. These results indicate that the Cognis/Bescorp system has been highly effective at remediating soils contaminated with trace metals.

Table 10
Terramet Acceptance Period Results at TCAAP

Metal	Cleanup Goal, ppm	Sampling Period 1	Sampling Period 2	Sampling Period 3	Sampling Period 4	Sampling Period 5	Sampling Period 6
Antimony	4	<1	<1	<1	< 1	<1	<1
Cadmium	4	0.8	1.8	<0.02	3.0	0.2	1.5
Chromium	100	3.5	0.6	2.6	6.0	5.0	5.0
Copper	80	23.7	12.6	9.8	12.7	16.1	11.3
Lead	300	19	60	30	<60	<60	38
Mercury	0.3	<0.02	0.04	0.03	<0.02	<0.02	0.3
Nickel	45	8.9	6.2	4.6	5.4	6	7.8
Silver	5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Note: after COGNIS, Inc. (1993).